Title
Drastic reduction in the surface recombination velocity of crystalline silicon passivated with catalytic chemical vapor deposited SiN_x films by introducing phosphorous catalytic-doped layer

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Description

I. INTRODUCTION

n-type crystalline silicon (c-Si) has recently become more and more attractive to photovoltaic research, raising forecast of switch from p-type to n-type c-Si solar cells on photovoltaic industry.1,2 Up to date, n-type c-Si solar cells are available, but their market share is at very low level (around 4%).3 Nevertheless, the highest-efficiency solar cell has been recorded for an a-Si/n-type c-Si heterojunction back-contact solar cell in 2014.3 n-type c-Si solar cells have many advantages for realizing higher conversion efficiency than p-type wafer cells, such as no light-induced degradation and less effect of metal impurities, and their market share will thus increase in the near future, along with decrease in their process costs.1,4 Excellent passivation technique is of great importance particularly in improving back-contact c-Si solar cell efficiency. High-efficiency solar cells require surface passivation films not only with high transparency but also with high passivation ability so that photo-generated carriers do not recombine at the c-Si surface.5 Catalytic chemical vapor deposition (Cat-CVD),6 also referred to as hot-wire CVD, promises potential applications in passivation technique for c-Si solar cells. The world’s best level of an surface recombination velocity (SRV) of 1.5 cm/s has been obtained for n-type c-Si wafers passivated with Cat-CVD SiNₓ/amorphous-silicon (a-Si) stacked layers.7 Cat-CVD can also be used to form a shallow phosphorous (P)-doped layer, called P Cat-doped layer, at a low substrate temperature, such as room temperature.8,9 The shallow P doped layer can induce field-effect passivation, which can significantly suppress the recombination of minority carriers at c-Si surface. Although the shallow doping can be realized by other techniques, such as plasma doping, atomic layer deposition of dopants, and molecular beam epitaxy,10–14 Cat-doping can significantly avoid damage onto c-Si surface induced by energetic ions since gas molecules are decomposed on a hot wire by catalytic reaction. The advantage makes Cat-doping become a favorable method for the formation of field-effect passivation layers for c-Si. Regarding the application of P Cat-doped layers to passivation technique, it has been already reported that the addition of P Cat-doped layers can reduce the SRV of n-type c-Si passivated with an a-Si film from 5 cm/s to 3 cm/s.15 In our previous work, we have optimized SiNₓ passivation films with refractive index of ~2.0 at wavelength of 630 nm prepared by Cat-CVD for n-type c-Si wafers.16 The highest effective minority carrier lifetime (τ_eff) of 3 ms, corresponding to a low SRV of 5 cm/s, can be obtained for n-type c-Si passivated with Cat-CVD SiNₓ films deposited at a low substrate temperature (~100°C) and post annealing. The use of SiNₓ films, whose refractive indexes are adjusted to be 2.0 even after decreasing the substrate temperatures, can avoid optical loss due to parasitic absorption in a-Si for SiNₓ/a-Si stacked passivation system. The Cat-CVD SiNₓ films with high passivation quality and high transparency are suitable for application to c-Si solar cells. As we mentioned above, a P Cat-doped layer can induce field-effect passivation, which is effective in suppressing surface recombination by sending electrons away from the c-Si surface. In this study, in order to obtain even lower SRV on c-Si surface passivated with a SiNₓ film, we attempt to apply P Cat-doping for field-effect passivation. The results obtained show that the passivation quality of the SiNₓ/P Cat-doped layer/c-Si structure significantly depends on the amount of activated donors in a P Cat-doped layer. Doped substrate temperature and annealing before depositing SiNₓ films are important parameters for...
activating P as donors. The deposition of SiNx films and post annealing at 350°C for 30 min are necessary to achieve better interface properties and resulting high $\tau_{\text{eff}}$.$^{16}$ By the field-effect passivation and defect termination by H atoms, $\tau_{\text{eff}}$ of as high as 7 ms can be obtained, which corresponds to an SRV of ~2 cm/s.

II. EXPERIMENTAL PROCEDURE

Sample preparation conditions are summarized in Table I. All c-Si wafers were first cleaned in diluted (5%) hydro-fluoric acid (HF) solution for 10 s to remove native oxide. P Cat-doped layers, SiNx, films, and a-Si films were prepared in separate Cat-CVD chambers. A 2.25% helium diluted PH$_3$ was used as gas source for doping process. In this study, we changed the properties of P Cat-doped layers by changing substrate temperature ($T_{\text{dope}}$) and doping time ($t_{\text{dope}}$). The deposition condition of SiNx films and annealing conditions for the samples after depositing the SiNx films were same as the optimized conditions, under which high $\tau_{\text{eff}}$ of 3 ms can be obtained for a SiN$_x$-c-Si structure.$^{16}$ 290–μm-thick n-type (100) floating-zone (FZ) Si wafers with a resistivity of 2.5 Ω cm and a bulk minority carrier lifetime of >10 ms were used for the investigation of the passivation quality. The structure for $\tau_{\text{eff}}$ measurement is shown in Fig. 1. In order to investigate the effect of annealing on passivation quality, the P Cat-doped samples were annealed before and after depositing SiNx films. In this paper, we refer them to “annealing A” and “annealing B,” respectively. Annealing A and annealing B were both conducted in a horizontal tubular furnace in nitrogen atmosphere. We prepared two samples under the same P doping condition at the same batch; one is for a sample with only annealing B, and the other is for a sample with both annealing A and B. The samples without annealing A were passivated with SiNx films immediately after P Cat-doping without any air break, while the samples with annealing A were taken out from the P doping chamber, followed by furnace annealing and then SiNx deposition without any additional cleaning prior to deposition. All the SiNx-deposited samples were finally annealed at 350°C for 30 min (annealing B). The $\tau_{\text{eff}}$ was measured by microwave photo-conductivity decay (μ-PCD) (KOBELCO LTA-1510EP) using a 904 nm wavelength pulse laser with a photon density of $5 \times 10^{10}$ cm$^{-2}$, and then was evaluated from the exponential decay of the microwave reflection intensity. The $\tau_{\text{eff}}$ was measured in position-dependent mapping mode, and $\tau_{\text{eff}}$ shown below is the maximum value in the $20 \times 20$ mm$^2$ area mapping. The relationship between $\tau_{\text{eff}}$ and SRV is described as

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2\text{SRV}}{W},$$

where $\tau_{\text{bulk}}$ and $W$ represent minority carrier lifetime in bulk c-Si and wafer thickness, respectively. In this study, we calculated SRV by assuming $\tau_{\text{bulk}} = \infty$. We also measured excess-carrier-density-(Δn−) dependent $\tau_{\text{eff}}$ by quasi-steady-state photoconductance (QSSPC) (WCT-120, Sinton Instruments).

We employed the Hall effect measurement to evaluate the sheet carrier density ($N_D$) of doped samples and secondary ion mass spectrometry (SIMS) for P concentration. The properties of c-Si wafers used for SIMS measurement are same as those used for $\tau_{\text{eff}}$ measurement. The SIMS measurement was performed from the back side of the samples after removing most of Si wafers in order to avoid the effect of knock-on and resulting unintentional broadening of P profiles. We used 2900 Ω cm p-type FZ c-Si wafers for the Hall effect measurement. The capture of carriers at defects on c-Si surface and oxidization may affect significantly the results of the Hall effect measurement.$^{8,17,18}$ In order to prevent these effects, a 10-nm-thick a-Si film was deposited on c-Si immediately after P doping without air exposure. In order to know the effect of annealing on $N_D$, samples were annealed at 350°C before and after depositing a-Si films. Four Al electrodes were formed by vaporization through a metal hard mask to form the van der Pauw configuration. The samples were annealed at 350°C for 1 min to make Ohmic contact between Al electrodes and a P Cat-doped layer. Figure 2 shows the cross-sectional schematic of a sample for the Hall effect measurement. The details of the measurement have been described in Ref. 8. The effect of H etching on the

| TABLE I. Sample preparation conditions for P Cat-doping and the deposition of SiNx and a-Si films. |
|---------------------------------|-----------------|-----------------|-----------------|
| **Doping** | **a-Si** | **SiNx** |
| Gas sources | PH$_3$; 20 sccm | SiH$_4$; 10 sccm | SiH$_4$; 8 sccm NH$_4$; 150 sccm |
| Substrate temperature | 80–300°C | 90°C | 100°C |
| Pressure | 1.0 Pa | 0.55 Pa | 10 Pa |
| Catalyzer temperature | 1300°C | 1800°C | 1800°C |
| Time | 30–120 s | 30 s | 184 s |

FIG. 1. The cross-sectional schematic of a sample for $\tau_{\text{eff}}$ measurement.
morphism of c-Si surface after P Cat-doping was evaluated by atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

A. The effect of annealing on P activation as donors and the passivation characteristic of SiNx/P Cat-doped layer/c-Si structures

Annealing plays an important role in improving the passivation quality of SiNx/c-Si structures. In this study, we first investigate the effect of annealing. c-Si wafers received P Cat-doping at a $T_{a-dope}$ of 80°C for 1 min, followed by SiNx film deposition. The samples were then annealed (annealing B) at various annealing temperatures ($T_{ab}$) for 30 min. Figure 3 shows the dependence of $\tau_{eff}$ of a SiNx/P Cat-doped layer/c-Si structure on $T_{ab}$. The $\tau_{eff}$ of SiNx/c-Si structures as a function of $T_{ab}$ is also shown for comparison. $\tau_{eff}$ starts to increase when $T_{ab}$ exceeds 200°C for both structures. $\tau_{eff}$ reaches the highest value at a $T_{ab}$ of 350°C, and then decreases with further increase in $T_{ab}$. The improvement in the $\tau_{eff}$ of the SiNx/c-Si structure is supposed to be due to the defect termination by H atoms during annealing. For a SiNx/P Cat-doped layer/c-Si structure, passivation quality relies not only on H defect termination but also on field-effect passivation, and increase in $T_{ab}$ might lead to increase in donor (activated P) concentration and resulting enhancement in field-effect passivation. Hayakawa et al. have reported that the most inactivated P atoms in a P Cat-doped layer exist in the forms of chemisorbed PH3, PH2, and PH3 (coordinate bond)-type bonds with Si atoms, denoted as PHx ($x = 1-3$). It has been reported that P and H atoms are major products, while PHx and PH2 are minor products in the catalytic decomposition of PH3. We thus guess that the extraction of H atoms from PH3 molecules by formation of H2 molecules or the addition of H atoms to P atoms on a c-Si surface is possible mechanisms of PHx production.

PHx may decompose at high temperature, resulting in the release of P and H atoms. The released H atoms can diffuse to c-Si surface and terminate defects there, and the released P atoms act as donors and contribute to reinforcing field-effect passivation. There have been a number of literatures about the decomposition of P-H bonds using samples with PH3 adsorbed on c-Si (100). Yu et al. have reported that PH3 molecules are partially dissociated at an annealing temperature of 275°C for PH3 adsorbed samples. Tsai et al. have reported that PH3 species are converted to PH2 species in an adsorbed layer at annealing temperature >317°C, and a P-H peak disappears when an annealing temperature exceeds 377°C. These facts indicate that PH2 species are decomposed to P and H atoms at around 300°C. We can guess that the released H atoms can make bonding with Si atoms and P atoms start to act as donors. In this study, as has been shown in Fig. 3, the $\tau_{eff}$ of a SiNx/P Cat-doped layer/c-Si structure is much higher than that of SiNx c-Si structure when $T_{ab} \geq 250°C$. This fact suggests that PHx starts to decompose efficiently at a $T_{ab}$ of 250°C. This temperature is quantitatively consistent with the values of the literatures shown above. A $T_{ab}$ of 350°C is sufficiently high for both PHx bond breaking in a P Cat-doped layer and defect termination by H in SiNx films, and higher $T_{ab}$ leads to the desorption of H atoms to atmosphere and resulting in the decrease of $\tau_{eff}$. The highest $\tau_{eff}$ can thus be obtained at a $T_{ab}$ of 350°C for both structures.

On the other hand, contrary to our expectations, the results of the Hall effect measurement show that $N_D$ decreases by annealing. $N_D$ is $1.2 \times 10^{12} \text{cm}^{-2}$ before annealing, while it reduces to $0.9 \times 10^{12} \text{cm}^{-2}$ for samples with annealing at 350°C for 30 min after depositing a-Si films, and to $0.7 \times 10^{12} \text{cm}^{-2}$ for samples with annealing at the same condition before depositing a-Si films. For the sample annealed after depositing an a-Si film, a possible reason for reduction in $N_D$ is the diffusion of H atoms from the a-Si film to the P Cat-doped layer, which can cause the formation of more PHx than PHx decomposition in a P Cat-doped layer and resulting reduction in $N_D$. Lower $N_D$ obtained in the sample annealed before depositing an a-Si film may be due to the oxidation of c-Si surface. In order to conduct annealing process, we have to take out the samples to atmosphere. Oxidation can inactivate P at surface c-Si and/or induce the formation of a thin Si oxide film containing P atoms on c-Si surface, which affect the results of the Hall effect measurement. In order to clarify this effect, the samples for the Hall effect measurement

![FIG. 2. The cross-sectional schematic of a sample for Hall measurement.]

![FIG. 3. The dependence of SiNx/P Cat-doped layer/c-Si structures on $T_{ab}$ at an annealing time of 30 min. $\tau_{eff}$ of SiNx/c-Si structures as a function of $T_{ab}$ is also shown for comparison.]

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after P Cat-doping at 350°C were put in air for 15 min before depositing a-Si films. By the additional air exposure, \( N_D \) drops from \( 3 \times 10^{12} \) to \( 0.5 \times 10^{12} \) cm\(^{-2} \), which is a clear evidence of oxidation-induced reduction in \( N_D \). We actually confirmed the formation of a SiO\(_x\) film with a thickness of 1.1 nm and a refractive index of 1.5 at a wavelength of 630 nm on c-Si surface by using spectroscopic ellipsometry.

However, the oxidation of c-Si surface does not deteriorate the passivation quality of SiN\(_x\)/P Cat-doped layers on c-Si structure. The P Cat-doped layer/c-Si structures with or without annealing A (at 350°C for 30 min) were put in air for one week. The sample was then passivated with a SiN\(_x\) film, and annealed at 350°C for 30 min (annealing B). For the sample without annealing A, \( \tau_{\text{eff}} \) obtained of 4.4 ms does not differ from \( \tau_{\text{eff}} \) of sample without air exposure. For the sample annealed with annealing B, \( \tau_{\text{eff}} \) obtained is 6.4 ms. The addition of annealing A rather improves the passivation quality of a SiN\(_x\)/P Cat-doped layer structure by oxidation. We also investigated the effect of oxidation on \( \tau_{\text{eff}} \) of SiN\(_x\)-passivated c-Si samples. Some c-Si wafers received annealing A at 350°C for 30 min in N\(_2\) atmosphere. The \( \tau_{\text{eff}} \) of SiN\(_x\)/c-Si structures increases from 50 to 100 \( \mu \)s for samples without annealing B and from 3 to 3.5 ms for samples with annealing B. This indicates that the thermal oxidation of c-Si surface slightly improves the passivation quality of SiN\(_x\) films on c-Si wafers. This improvement may be due to reduction in interface state by the formation of a SiO\(_x\) film. Furthermore, \( \tau_{\text{eff}} \) of 250 \( \mu \)s is obtained for SiN\(_x\)/P Cat-doped layer/c-Si structure with only annealing A. This value is higher than that of a SiN\(_x\)/c-Si structure annealed with only annealing A. This result indicates that despite reduction in \( N_D \) by oxidation, improvement in interface quality by oxidation and defect termination by H atoms released from PH\(_x\) can contribute to increase in \( \tau_{\text{eff}} \). After annealing B, besides the effect of defect termination by H atoms diffused from a SiN\(_x\) layer, more PH\(_x\) in a P Cat-doped layer can be decomposed, leading to higher donor concentration and more effective defect termination by H atoms, which results in higher \( \tau_{\text{eff}} \).

On the other hand, as mentioned previously, \( N_D \) obtained for an a-Si/P Cat-doped layer/c-Si structure is reduced by annealing at 350°C for 30 min. Cat-CVD SiN\(_x\) films also contain high amount of H atoms, which can diffuse from SiN\(_x\) films to c-Si surface and terminate defects or recombine with P atoms to form more PH\(_x\) during annealing B. Assuming that reduction in \( N_D \) for the SiN\(_x\)/P Cat-doped layer/c-Si structures is the same as the case of a-Si/P Cat-doped layer/c-Si after annealing B, \( N_D \) of a SiN\(_x\)/P Cat-doped layer/c-Si structure decreases by 25%. The sample undergoing both annealing A and B has \( N_D \) of \( \sim 5 \times 10^{11} \) cm\(^{-2} \), which is due to the effect of oxidation by annealing A and H diffusion during annealing B. This value of \( N_D \) might be high enough for field-effect passivation. The fact that the \( N_D \) of the sample receiving both annealing A and B is less than that with only annealing B indicates less effective field-effect passivation. However, the benefit of defect termination by H atoms might overcome the deterioration of field effect and lead to better \( \tau_{\text{eff}} \) for the sample with both annealing A and B.

To understand the effect of annealing A on the passivation quality of SiN\(_x\)/P Cat-doped layers, c-Si samples Cat-doped at 80°C for 1 min were annealed (annealing A) at various annealing temperatures (\( T_{\text{aA}} \)) for 30 min in the tubular furnace. Samples were then moved to the Cat-CVD system to deposit SiN\(_x\) films. Finally, samples were annealed at 350°C for 30 min (annealing B). Figure 4 shows the \( \tau_{\text{eff}} \) of SiN\(_x\)/P Cat-doped layer/c-Si structures after annealing A and B as functions of \( T_{\text{aA}} \) and annealing time \( (t_{\text{aA}}) \) for annealing A. \( N_D \) as a function of \( T_{\text{aA}} \) is also shown. One can clearly see that \( \tau_{\text{eff}} \) increases with \( T_{\text{aA}} \) and decreases when \( T_{\text{aA}} \) increases. The increase in \( N_D \) is probably due to the decomposition of PH\(_x\) at higher \( T_{\text{aA}} \) and resulting activation of higher amount of P atoms. Additionally, the thermal oxidation of c-Si surface for the samples annealed at high temperature and defect termination by H atoms by annealing might contribute to the formation of a high-quality SiN\(_x\)/SiO\(_x\)/P Cat-layer and c-Si interface, resulting improvement in \( \tau_{\text{eff}} \). Because the P Cat-doped layer is very shallow, too high \( T_{\text{aA}} \) might lead to the desorption of H and P atoms to environment, which can result in decrease in \( \tau_{\text{eff}} \) due to less effective defect termination and field-effect passivation. The complete

![Figure 4](image-url)
thermal desorption of P atoms from PH₃ adsorbed c-Si surface at high temperature above 550 °C was also reported in Ref. 24, in which the desorption of H atoms at 400 °C has also been observed. The same tendency is seen in the annealing time dependence for annealing A, as shown in Fig. 4(b). T_{taA} of 400 °C and t_{taA} of 30 min are thus optimum conditions for annealing A needed to activate P in P Cat-doped layer without H and P desorption, and the highest t_{eff} obtained for SiNx/P Cat-doped layer/c-Si structures under the conditions. Figure 5 shows t_{eff} as a function of the duration of annealing B (t_{taB}). We can see that t_{eff} is still high for long t_{taB}. The tendencies of the variation of t_{eff} for both samples are the same. Annealing for 30 min is enough to obtain high passivation quality for the samples. Further increase in t_{taB} does not enhance more the activation of P atoms as well as defect termination. The instability of t_{eff} due to increase in T_{taB} and t_{taB} may raise a doubt of reduction in t_{eff} after long time exposure to air even at room temperature. We have confirmed that t_{eff} of both SiNx/c-Si and SiNx/P Cat-doped layer/c-Si structures remain original values even after putting in air at room temperature for about 10 months.

In summary, a remarkably high t_{eff} of ~7 ms, which corresponds to an SRV of ~2 cm/s, can be achieved for SiNx/P Cat-doped layer/c-Si samples after annealing A and B. Compared with a SiNx/c-Si structure, the insertion of P Cat-doped layer can reduce an SRV from 5 cm/s to 2 cm/s. The SRV of 4 cm/s has also been achieved when nearly stoichiometric SiNx films were deposited by plasma-enhanced CVD (PECVD) on 150-μm-thick 3–5 Ω cm n-type Czochralski (Cz) Si wafers after annealed in an industrial firing process. An SRV of lower than 10 cm/s has been reported for 1.5 Ω cm p-type Si wafers passivated with stoichiometric SiNx films. In these reports, they calculate SRV through t_{eff} obtained by a contactless photoconductance tester allowing both transient PCD and QSSPC measurements at an Δn of 1 x 10^{15} cm⁻³. Figure 6 shows t_{eff} of a SiNx/P Cat-doped layer/c-Si structure and a SiNx/c-Si structure measured by QSSPC in transient mode. We observed t_{eff} of ~7 ms for SiNx/P Cat-doped layer/c-Si structure and ~3 ms for SiNx/c-Si structure at a Δn of 2.4 x 10^{15} cm⁻³. At a Δn of 1 x 10^{15} cm⁻³, t_{eff} is ~4 and 1.8 ms for SiNx/P Cat-doped layer/c-Si and SiNx/c-Si structures, corresponding to SRVs of 3.6 and 8 cm/s, respectively. Our SRV obtained in this study is the lowest level for n-type c-Si passivated with SiNx films without firing process or with only low temperature process, which is acceptable for fabrication of a-Si/c-Si hetero-junction solar cells. The remarkable value of our SRV obtained for SiNx/P Cat-doped layer/c-Si structure highlights the promising application of Cat-CVD technique in high-efficiency n-type c-Si based solar cell fabrication.

B. Effect of Ts-dope and doping duration on the passivation characteristic of SiNx/P Cat-doped layer/c-Si structure

High Ts-dope can activate P atoms as donors in a P Cat-doped layer. This can contribute to improvement in field-

FIG. 5. t_{eff} of SiNx/P Cat-doped layer/c-Si structures with and without annealing A as a functions of t_{taB} at a T_{taB} of 350 °C. Annealing A was conducted at 400 °C for 30 min.

FIG. 6. t_{eff} as a function of excess carrier density in a SiNx/P Cat-doped layer/c-Si structure and a SiNx/c-Si structure.

FIG. 7. t_{eff} of SiNx/P Cat-doped layer/c-Si samples as a function of T_{s-dope}. N_{_{3}} as a function of T_{s-dope} before annealing A is also shown. Annealing A was conducted at 400 °C for 30 min and annealing B was conducted at 400 °C for 30 min.
effect passivation. In this investigation, we prepared P Cat-doped samples at various $T_{s\text{-dope}}$ for 1 min. Figure 7 shows $\tau_{\text{eff}}$ of SiN$_x$/P Cat-doped layer/c-Si samples as a function of $T_{s\text{-dope}}$ with and without annealing A. $N_D$ as a function of $T_{s\text{-dope}}$ before annealing is also shown. $N_D$ increases with increase in $T_{s\text{-dope}}$. This may suggest that H atoms desorb from c-Si surface during P Cat-doping at high $T_{s\text{-dope}}$ due to the extraction of adsorbed H atoms on c-Si surface by atomic H and/or PH$_3$. As we mentioned above, Umemoto et al. have reported that major products in the catalytic decomposition of PH$_3$ molecules on a heated tungsten catalyzer are P and H atoms. Here, we suppose that the reaction of atomic H with adsorbed H and/or PH$_x$ on a c-Si surface and/or PH$_x$ bond breaking are possible mechanisms for H release at high $T_{s\text{-dope}}$. This process might assist P activation. We can see lower H concentration in a sample doped at a $T_{s\text{-dope}}$ of 300 °C in a SIMS profile, as shown in Fig. 8 later. The increase in $N_D$ makes small increase in $\tau_{\text{eff}}$ before annealing. It contributes significantly to improvement in $\tau_{\text{eff}}$ for the sample doped at high $T_{s\text{-dope}}$ when the samples were annealed with annealing B. The samples doped at a $T_{s\text{-dope}}$ of 300 °C, which shows $N_D$ of $\sim 2 \times 10^{12}$ cm$^{-2}$, can reach the highest $\tau_{\text{eff}}$ of $\sim 6$ ms.

Figure 7 also shows $\tau_{\text{eff}}$ of SiN$_x$/P Cat-doped layer/c-Si samples with annealing A and B as a function of $T_{s\text{-dope}}$. One can see that $\tau_{\text{eff}}$ does not depend on $T_{s\text{-dope}}$, and all the
samples have constant and high $\tau_{\text{eff}}$ of 7 ms. This result suggests that P donor concentration is constant in all the samples with annealing before and after SiNx deposition. Figure 8 shows the SIMS profiles of samples with P Cat-doping at $T_s$, dope of 80 and 300°C before annealing. We can see no significant difference in the two profiles, suggesting that the activation ratio of P atoms in the two samples is similar.

$N_D$ of a P Cat-doped layer also increases with $t_{\text{dope}}$. We should therefore concern the effect of doping time on $\tau_{\text{eff}}$ of SiNx/P Cat-doped layer/c-Si samples. The samples were doped at 80°C for 30, 60, 90, and 120 s. The effect of annealing before depositing SiNx films was also investigated for these samples. Figure 8 shows the $\tau_{\text{eff}}$ of SiNx/P Cat-doped layer/c-Si samples as a function of $t_{\text{dope}}$ with and without annealing at $N_D$. Although $N_D$ increases with increase in $t_{\text{dope}}$, $\tau_{\text{eff}}$ decreases when $t_{\text{dope}} > 60$ s. For the sample doped for 30 s, $\tau_{\text{eff}}$ is low due to low $N_D$. A possible reason for the low $\tau_{\text{eff}}$ observed in the samples with $t_{\text{dope}} > 60$ s is the effect of surface etching by radical species during Cat-doping process. Figure 10 shows the surface AFM images of bare c-Si and c-Si doped for 60 s and 90 s. The surface of bare c-Si has a root-mean-square roughness ($R_{\text{rms}}$) of ~0.09 nm with the average height of 0.3 nm. As shown in Figs. 10(b) and 10(c), the two P Cat-doped samples have more roughened surfaces, and the surface receiving longer Cat-doping is more seriously etched. The sample with a $t_{\text{dope}}$ of 90 s has a $R_{\text{rms}}$ of 0.24 nm and average height is 0.9 nm, while they are 0.21 nm and 0.7 nm, respectively, for the sample doped at 60 s. Excess $t_{\text{dope}}$ thus rather deteriorates the interface quality, and an optimum $t_{\text{dope}}$ exists to obtain high $\tau_{\text{eff}}$ for SiNx/P Cat-doped layer/c-Si structure.

IV. CONCLUSION

In conclusion, an extremely low SRV of 2 cm/s can be obtained for the SiNx/P Cat-doped layer/n-c-Si structure. Annealing plays important roles for improving the passivation quality of SiNx films and enhancing field-effect passivation. Additional annealing, before depositing SiNx films (annealing A), enhances the activation of P dopants in a P Cat-doped layer and improves $\tau_{\text{eff}}$. Increase in $T_{s,dope}$ increases sheet carrier density, resulting in the improvement of $\tau_{\text{eff}}$. $\tau_{\text{eff}}$ of SiNx/P Cat-doped/c-Si sample decreases with excessive $t_{\text{dope}}$ due to etching effect by radical species during P Cat-doping. An SRV of 2 cm/s is obtained under optimum Cat-doping and annealing conditions for SiNx films on n-type c-Si wafers, indicating the potential application of Cat-CVD in producing high-efficiency c-Si solar cells. We emphasize that the use of a high transparent SiNx passivation layer with a P Cat-doped layer can enhance the performance of n-type c-Si solar cells, particularly of back-contact solar cells.

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